# English translation of D1

#### 1. Title of invention:

A method for staining a water-containable contact lens and a stain solution used for the method

#### 2. What is claimed is:

- (1) A method for staining a water-containable contact lens having an amide group with a vat dye characterized in that polyethylene glycol is caused to be present in a stain solution containing the vat dye.
- (2) The method for staining a water-containable contact lens according to claim (1), wherein the state of said water-containable contact lens is made hydrous and said staining operation is carried out by a screen printing method.
- (3) The method for staining a water-containable contact lens according to claims (1) or (2), wherein said water-containable contact lens to which the stain solution is applied is subjected to an oxidation treatment with air or a dissolved oxygen in water.
- (4) A stain solution for staining a water-containable contact lens having an amide group characterized in that said stain solution contains a given vat dye, an alkaline chemical, a reducing agent and further polyethylene glycol.
- (5) The stain solution for staining a water-containable contact lens according to claim (4), wherein said stain solution contains 5 to 60 wt% of said polyethylene glycol.

# 3. Detailed description of the invention

#### (Technical field)

The present invention relates to a method for staining a water-containable contact lens with a vat dye, as well as a stain solution used for such a method.

### (Background art)

Staining a contact lens has numerous characteristics, for example, in that it is useful for glare protection; that it is easy to find the contact lens if it is dropped; and that it is possible to strengthen a brand image.

A normal contact lens, especially a soft contact lens is larger than a cornea. If the whole area of the contact lens is stained, a white sclerotic coat is partly seen stained, and therefore somebody else can easily recognize that the contact lens is being worn. Therefore, in general, during or after lens molding, only the desired part of the lens is stained or the whole of it is thinly stained with a reactive dye or a vat dye in order to carry out a desired staining.

In this connection, in view of the wearability and safety of a contact lens, a water-containable contact lens which is made softer by absorbing water has been developed and furthermore a soft contact lens achieving a water content of 40% or more has become commonplace. In general, as a water-containable component of the soft contact lens, a monomer having an amide group, such as N-vinyl pyrrolidone and N,N-dimethyl acrylamide is used as one copolymerizable component of the polymer constituting the lens.

However, a water-containable lens material having an amide group which is obtained from a polymer derived from copolymerization of such water-containable monomer cannot react with a reactive dye, and therefore the reactive dye cannot be used for staining such lens. Furthermore, such lens material has a high water content and such lens is easy to elute by, e.g. boiling. Therefore, it seems advantageous that a vat dye which is difficult to elute from the lens be used for staining the lens. However, staining the water-containable contact lens with such vat dye, on the basis of a method used in the field of normal dyeing fibers, produces a dyeing irregularity and therefore cannot uniformly stain the lens.

### (Problem to be solved)

In view of such circumstance, the present invention has been created. The purpose of the present invention is to provide a method for uniformly staining a water-containable contact lens having an amide group with a vat dye and a stain solution to be used for the method.

### (Means for solving the problem)

In order to solve the above problem, the present invention uses polyethylene glycol in a stain solution containing a vat dye when a water-containable contact lens having an amide group is stained with the vat dye.

In this connection, in such method for staining a water-containable contact lens, in general, the state of such water-containable contact lens is made hydrous and said staining operation is carried out by a screen printing method. Furthermore, the water-containable contact lens to which the stain solution is applied is subjected to an oxidation treatment with air or a dissolved oxygen in water and the vat dye becomes insoluble in order to stain the lens in a desired color phase.

Furthermore, the present invention also provides a stain solution to be used for such staining. That is, such a stain solution for a water-containable contact lens is for staining a water-containable contact lens having an amide group and contains a given vat dye, an alkaline chemical, a reducing agent and further polyethylene glycol. Furthermore, 5 to 60 wt% of polyethylene glycol is present in the stain solution.

Meanwhile, the present invention has been developed on the basis of the discovery that it is better that a glue component be used in a stain solution when a water-containable contact lens having an amide group is stained with a vat dye, and that polyethylene glycol is the best glue component. In this connection, the advantages of containing or adding such glue component to a stain solution are, for example, as follows;

- (a) A viscosity of the stain solution becomes high and therefore bleeding does not occur when silk screen is used during the staining of the lens;
- (b) A flow property of the stain solution becomes small, and accordingly, air oxidation is difficult to proceed and it is easy to handle the operation and stable and uniform staining is carried out.

The inventors of the present invention have studied various well-known glue materials, such as polyethylene glycol, sodium alginate and polyvinyl pyrrolidone, and found that polyethylene glycol is the best glue material. In this connection, when sodium alginate was used, it was found that it is easy to produce a dyeing irregularity and un-dyed portion. It

seems that this is because alginic acid formed a complex together with the amide group of a lens material. When polyvinyl pyrrolidone was used, staining could not be carried out and thus the intended color phase could not be obtained. It seems that this is because polyvinyl pyrrolidone formed a complex together with a reductant of a vat dye, which prevented the reductant from moving to the lens material. Furthermore, the other glue components were studied; however, it was found that these other glue components precipitated under a strong alkali condition, which is necessary for a stain solution, and a dyeing irregularity and un-dyed portion were produced, and they cannot be used.

In the present invention, polyethylene glycol which is used as a glue component, in general, is present in an amount of 5 to 60 wt% in a stain solution, thereby a good staining of a lens material can be attained. connection, when the concentration of polyethylene glycol in the stain solution is too low, a dyeing irregularity and leak are apt to be caused and therefore there is case where a lens cannot be uniformly stained. the concentration is too high, there is a case where a lens material cannot be Furthermore, a concentration of polyethylene glycol should be adjusted in accordance with its molecular weight. It is desirable that polyethylene glycol be used in a slightly high concentration when the molecular weight of polyethylene glycol is low. It is desirable that polyethylene glycol be used in a slightly low concentration when the molecular weight of polyethylene glycol is high. For example, it is desired that polyethylene glycol having a molecular weight of about 600 be used at 10 to 60 wt%, whereas polyethylene glycol having a molecular weight of about 20,000 be used at 5 to 40 wt%.

A vat dye added to the stain solution for staining a lens material according to the present invention is arbitrarily selected and used in accordance with the intended color phase. Most vat dyes, such as vat orange 1, 2, 3, 5, 7, 13; vat yellow 2; vat red 1, 10, 13; vat blue 3, 4, 5, 6; vat green 1, 3; vat brown 3, 9, can be used. The concentration of such vat dye is arbitrarily adjusted in accordance with the kind of vat dyes, the intended color phase, the concentration of another base material (compounding agent), and the vat dye is used at a concentration wherein a vat dye is uniformly reduced and dissolved. In general, a vat dye is added to the stain solution at about 0.001 to 10 wt%.

Furthermore, in the same manner as the conventional manner, a stain solution arbitrarily contains an alkaline chemical (base material) and a reducing agent, such as sodium hydroxide and sodium hydrosulfite (sodium dithionite) in order to reduce a vat dye and therefore make it water soluble. If the amount of these additives to be used is too small, it is difficult to reduce and dissolve a vat dye. If the amount of these additives to be used is too much, a vat dye precipitates by salting-out. Therefore, in the same manner as the conventional manner, the alkaline base material and reducing agent are added and used in an amount of 0.1 to 10 wt%.

An objective staining is carried out with a stain solution produced as mentioned above, that is, the stain solution containing a given vat dye, an alkaline chemical, a reducing agent and polyethylene glycol. In such a case, any water-containable contact lens (material) having an amide group, which is heretofore well-known, is used as a lens material to which such stain solution is applied. For example, a lens material composed of a polymer obtained by copolymerization of a water-containable monomer such as N-vinyl pyrrolidone and N,N-dimethyl acrylamide is exemplified. The state of this lens material is made hydrous before staining a desired area of the lens and the lens is subjected to a staining operation.

In the staining operation according to the present invention, any staining mean for a lens material which is heretofore well-known can be For example, a screen printing method which is described in JP-A-57-120912, an attachment jig method which is described in JP-A-62-73228, a method using a porous stamp which is described in JP-A-53-45253, and a transfer method using a silicone pad, can be used. staining for a given area of a lens material is carried out in accordance with Especially, it is recommended that a screen each staining method. printing method be selected in view of ease of staining. In this connection, such staining operation can be, as is conventionally done, carried out at 0 to 100°C. In general, it is recommended that such staining operation be carried out at a temperature around room temperature, in view of ease of operation.

In this connection, a lens material impregnated with the stain solution

of the present invention is oxidatively-treated, a water-soluble vat dye (leuco compound) is oxidized and thus the original dye is insolubilized in the lens material in order to stain the lens. In this connection, this oxidization is readily carried out with oxygen in air or a dissolved oxygen in water. Specifically, the oxidization is carried out by leaving the lens containing the stain solution in air or by a boiling treatment in hot water. In the present invention, since the oxidization is accelerated by heating, a heating process for a lens material containing the stain solution is preferably selected.

### (Examples)

Several examples are indicated as follows in order to more specifically explain the present invention. However, the scope of the present invention should not be limited by the examples.

In this connection, every "part" and "%" in Examples are based on weight.

Furthermore, it should be understood that the present invention can be changed, modified and improved, so long as there is no departing from the purpose of the present invention, on the basis of the technical knowledge of a person skilled in the art. Therefore, it should be understood that the present invention is not limited to only the following Examples and the above specific description.

# Example 1

2g of sodium hydroxide, 2g of sodium hydrosulfite, 1g of blue 204 (vat dye) and 95g of a distilled water were fed into a 100ml vial container, which was sealed off and was shaken to agitate the contents for 2 hours at room temperature in order to obtain liquid A. On the other hand, 80g of a distilled water was added to 20g of polyethylene glycol (molecular weight: 20,000) in order to obtain liquid B. 10g of liquid A was mixed with 30g of liquid B, the resultant mixture was poured into an injection syringe and air was removed.

On the other hand, 85 parts of N-vinyl pyrrolidone, 14.8 parts of methyl methacrylate and 0.1 part of allyl methacrylate were polymerized in the presence of 0.1 part of azobisisovaleronitrile and the resultant polymer was moulded in order to obtain a water-containable soft contact lens (a lens

material). The state of this contact lens was made hydrous, the lens was attached to a silk screen treated so as to stain only a desired part of the lens and a tag was fixed to the lens.

Then, the stain solution in the injection syringe was dropped on the opposite side of the screen. After leaving it to stand for several minutes, the stain solution was washed out and the lens material was put into distilled water and boiling treatment was made to the lens for 1 hour. As a result, it was found that the desired area of the lens was uniformly stained blue.

In this connection, the stained lens and water were fed into a vial container and the vial container was sealed off and left on a house top for one month in order to expose it to sunlight, but no color degradation of the lens was found. The stained lens was immersed in saline and subjected to boiling treatment for 200 hours but no color degradation of the lens was found.

# Comparative Example 1

Staining a lens material was carried out as in Example 1, except that a solution containing 10g of sodium alginate (500cps) and 90g of distilled water was used as liquid B and the lens was left in a drying machine at 50°C for 10 mins after the stain solution in the injection syringe was dropped on the screen. As a result, it was found that the stained area of the lens material had a dyeing irregularity and lack.

# Comparative Example 2

Staining a lens material was carried out as in Example 1, except that a polyvinyl pyrrolidone (West Germany, BASF, Kollidon 90) 10% aqueous solution was used as liquid B. However, it was found that the lens material was not stained at all.

### Example 2

Staining a lens material was carried out as in Example 1, except that a soft contact lens which was made by polymerization of 40 parts of N-vinyl pyrrolidone, 45 parts of N,N-dimethyl acrylamide, 14.8 parts of methyl methacrylate and 0.1 part of ethylene glycol dimethacrylate in the presence

of 0.1 part of azobisisobutyronitrile was used. It was found that the desired area of the lens was uniformly stained blue.

# Example 3

Staining a lens material was carried out as in Example 1, except that 2g of vat green 3 was used as a dye and, after the stain solution was dropped on the screen, the lens was left in a drying machine at 50°C for 3 mins in order to accelerate impregnation of the stain solution. The obtained lens material was uniformly stained green. Furthermore, the color degradation test was carried out in the same way as in Example 1. Thus, no color degradation was found.

### Example 4

Staining a lens material was carried out as in Example 1, except that 2g of vat red 10 was used as a dye, and that liquid B prepared by adding 60g of distilled water to 40g of polyethylene glycol (molecular weight: 1,000) and dissolving it in water. It was found that the staining operation resulted in the lens material being uniformly stained red. Furthermore, the color degradation test was carried out in the same way as in Example 1. No color degradation was found.

### (Effect by the invention)

As is clear from the above explanation, in accordance with the present invention, staining of a water-containable contact lens having an amide group with a vat dye is advantageously carried out in the presence of polyethylene glycol as a glue component in a stain solution and thus a stained lens having excellent uniformity can be obtained.